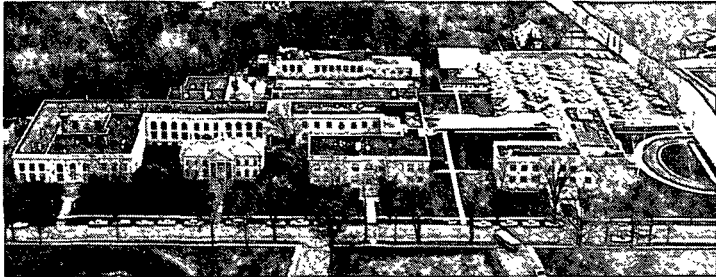


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ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS (II):
ELECTROCHEMISTRY OF ANTHRAQUINONE/LIGNIN MODEL QUINONEMETHIDES

DONALD R. DIMMEL, LOIS F. PERRY, PETER D. PALASZ,
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APRIL, 1984

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GENERAL SUMMARY

Institute Project 3475 has been concerned with developing a fundamental understanding of the reactions occurring during pulping and bleaching. One phase of this project research has involved a detailed investigation of the mechanism of action of anthraquinone (AQ) as a pulping catalyst. The attached article is the second of a series; the first was published as IPC Technical Paper No. Series 139. The work described herein was a joint research effort between us and a group of scientists at the Solar Energy Research Institute in Colorado. The group at SERI have been performing electrochemical experiments on lignin and other pulping by-products.

By means of electrochemistry, we have generated partially-reduced and fully-reduced forms of anthraquinone and have shown that these forms can transfer electrons to lignin model quinonemethides, causing the latter to fragment. Direct electron transfer from an electrode (during electrolysis) to quinonemethides can also be promoted and again the quinonemethides fragment. Fragmentation of lignin quinonemethides is presumed to be a key step in chemical pulping.

Our electrochemical experiments demonstrate a hitherto unknown type of chemistry, electron transfer reaction, which is probably occurring during anthraquinone pulping and possibly in other pulping systems. Our results suggest that pumping electrons (of the right voltage) into pulping systems, by means of additives, electric currents or whatever, should increase pulping rates.

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ABSTRACT

Electron transfer reactions have been observed during the electro-
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model quinonemethides. In dry acetonitrile at a reduction poten-
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reduced directly at the electrode at this potential but are
reduced by AHQ⁻ to give quinonemethide radical anions (QM⁻) and
AQ. The QM⁻ species rapidly fragment at their β -aryl ether bond
to give phenolate ions and radicals; the latter further reduces to
another phenolate ion. For example, the β -methyl lignin model QM
1 gives guaiacol and isoeugenol upon electrolysis at $-0.9V$ in the
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leads to both anthrahydroquinone radical anion and dianion; the
dianion is formed by direct electrolysis of the radical anion and
by disproportionation of the radical anion. Under all conditions
and substrates examined, electron transfer reactions proceeded in
preference to bond formation reactions which would generate
"adducts." The implication of these results is that it should be
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anthraquinone probably functions this way.

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^bPostdoctoral Fellow under the Director's Development Fund.

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linearly at potential scan rates ranging from 0.02 to 100 V/sec in the cathodic (reduction) direction from zero time (0 volts vs. Ag/AgCl) to a switch time (for example at -2.0 V), after which the potential is linearly returned (anodic direction, oxidation) to the starting (0 V) potential. The potentials, unless stated otherwise, are referenced against a Ag/AgCl electrode.

Appreciable current flow is only observed at extreme potentials where the solvent (or supporting electrolyte) is being reduced or oxidized, and in the vicinity of the formal electrode potential of an electroactive substance. The electrochemical domain of the solvent/supporting electrolyte system depends on the specific nature of the ionic species present in the solvent and on the nature of the solvent. Background currents exist because of electrochemical reactions of trace impurities in the system and because of the double-layer charging current. Typical background currents are shown by the dotted lines in Fig. 1.

The magnitude of the observed current during cyclic voltammetry is related to the potential scan rate, the number of electrons being transferred to (or from) the substrate, the concentration of the substrate, the area of the electrode, the rate of electron transfer to (or from) the electrode, and the rate of diffusion of the substrate to the electrode. The solution is not stirred during cyclic voltammetric experiments, and thus only a very small quantity of the substrate, that which is within 10-15 angstroms of the electrode, is electrolyzed. By stirring between runs, identical voltammograms can be obtained.

CYCLIC VOLTAMMETRY OF ANTHRAQUINONE

A cyclic voltammogram of anthraquinone (AQ) in DMSO with 0.1M tetrabutylammonium perchlorate (TBAP) is shown in Fig. 1. The voltammogram displays two well-separated cathodic (reductive) current peaks in the range of 0 to -2.0 V. The first current peak occurs at a cathodic peak potential of -0.78 V and corresponds to the one-electron, reversible, diffusion controlled, heterogeneous

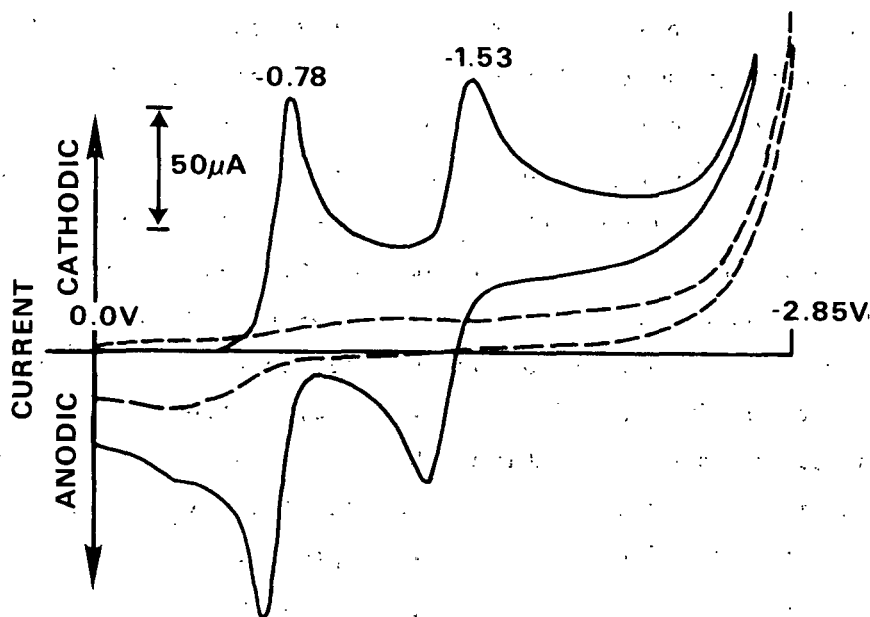


Figure 1. Cyclic voltammogram of AQ (2.3 mg) in DMSO (10 mL, 0.1M TBAP); potential scan rate of 0.5 V/sec.

electron transfer from the cathode to anthraquinone, leading to anthrahydroquinone radical anion; the second current peak at a cathodic peak potential of -1.53 V corresponds to the reduction of the radical anion to the dianion. Upon reversal of potential, two anodic (oxidation waves) are observed; these correspond to the reversal of the one-electron steps mentioned above. In acetonitrile the cathodic peak potentials are located at -0.92 V and -1.72 V.

The most useful solvents for electrochemical studies of radical anions are dimethylsulfoxide (DMSO), acetonitrile (AN), dimethylformamide (DMF), acetone and dimethoxyethane.^{3,4} In general, the electrochemically generated radical anions and, to some extent, dianions are relatively stable in these solvents. The electrode potential of polar substances, such as quinones, are affected by solvent changes and by association with nonaqueous electrolytes (substrate radical anions association with supporting electrolyte cations). The observed electrochemical behavior often changes when proton donors, such as water, phenol, and acetic acid, are added to aprotic solvents, such as AN and DMSO; protonation of ionic intermediates is possible.⁵

Addition of 7% by volume of water to AN causes the two AQ cathodic waves to collapse to one wave at -0.95 V (Fig. 2). The intensity is about the same as that of the cathodic reduction in dry acetonitrile. The corresponding anodic current peak occurs at -0.63 V. With 2% water the two waves are not completely collapsed, but the second cathodic wave shifts anodically (Fig. 2). These curves are explained by the reduction of AQ to $AHQ^{\cdot-}$ and the disproportionation of the latter species into AQ and AHQ^{2-} , as well as by protonation and reduction of the anionic species.^{3,5}

The behavior of anthraquinone and related compounds in aqueous solutions as a function of pH and the nature of the buffer system has been studied previously using polarography.⁶ The polarographic technique employs a dropping mercury working electrode and much slower potential scan rates than those used in cyclic voltammetry. The polarographic behavior of AQ in water ranges from two one-electron processes with two well separated waves to single waves close to the behavior expected for a two-electron process. Strong influence of the buffer composition and of the pH was observed (parallel to that observed in nonaqueous solvents for the effect of the supporting electrolytes). The polarographic behavior can be explained by two one-electron reductions coupled to two major chemical reactions - the dimerization of the radical anions and their disproportionation; the observed behavior depends on the relative rates of the various reactions and is a function of the solvent/supporting electrolyte.

In summary, the cyclic voltammetry of AQ in either AN or DMSO shows two well-separated one-electron reductions (waves) which are reversible. The addition of small amounts of water causes the second wave to shift to more positive potentials which coincide with the first wave.^{3,5}

CYCLIC VOLTAMMETRY OF QUINONEMETHIDES

Quinonemethides (QMs) are key reactive intermediates in many lignin transformations.¹ The stability of simple QMs in nucleo-

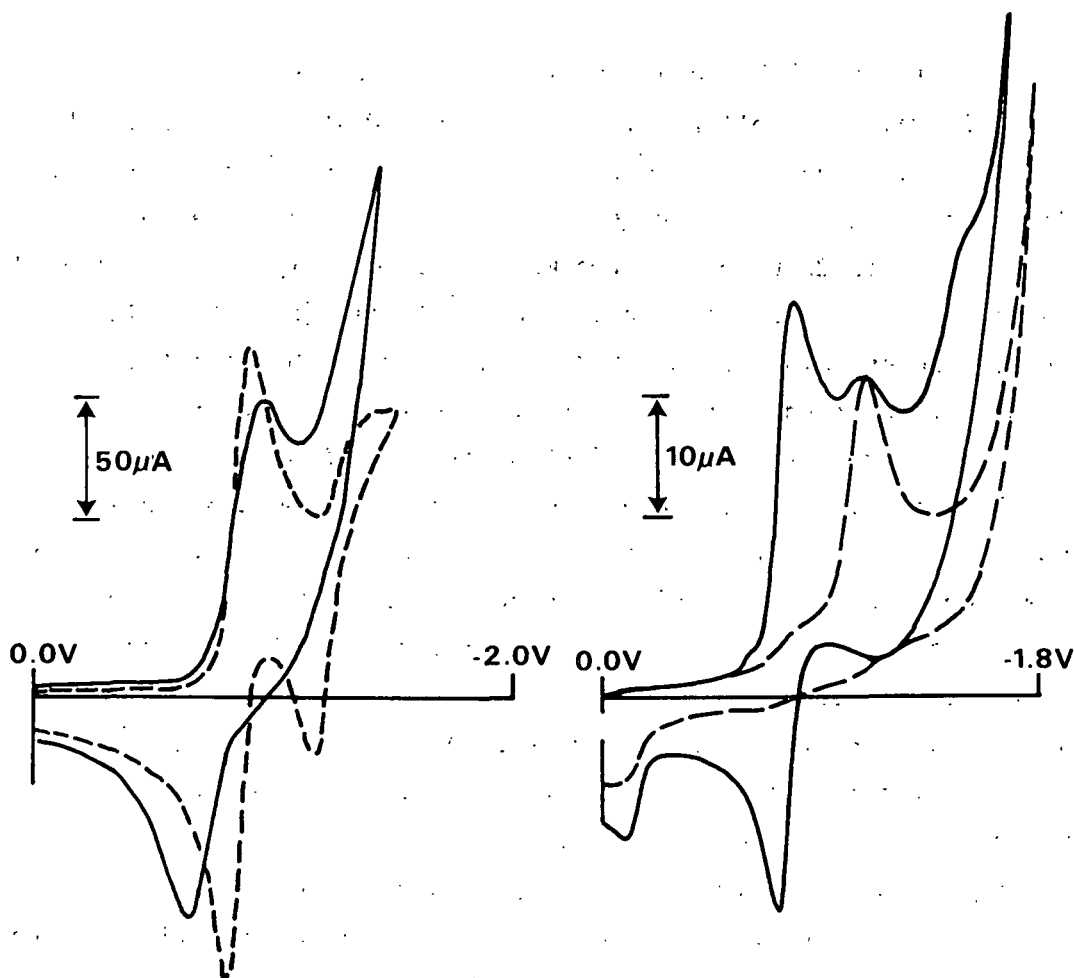


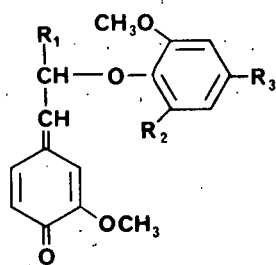
Figure 2. Cyclic voltammogram of AQ (2.5 mg) in AN (10 mL, 0.1M TBAP) in the presence of water (---, 2% v/v; —, 7% v/v); potential scan rate of 0.2 V/sec.

Figure 3. Cyclic voltammogram of QM 1 (1.5 mg in 0.2 mL CHCl₃) in DMSO (10 mL, 0.1M TBAP) alone (---, A) and in the presence of AQ (—, B); potential scan rate of 0.2 V/sec.

philic solvents such as water is extremely short, a matter of seconds at room temperature.⁷ However, more highly substituted, sterically crowded QMs, similar to those found in lignin, have much longer lifetimes (ca. weeks) in the absence of good nucleophiles or water.^{8,9}

Starting from compounds 4-6 and following the directions of Ralph and coworkers,^{8,9} we have prepared and characterized stable CHCl₃ solutions of quinonemethides 1-3. Attempts to prepare stable solutions of simple QMs 7 and 8 by a similar procedure failed.

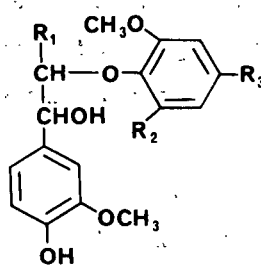
These QMs are probably rapidly destroyed by a water extraction used in the procedure.



1, $R_1 = \text{CH}_3, R_2 = R_3 = \text{H}$

2, $R_1 = R_3 = \text{CH}_3, R_2 = \text{OCH}_3$

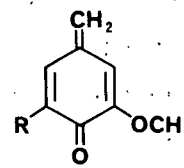
3, $R_1 = R_2 = R_3 = \text{H}$



4, $R_1 = \text{CH}_3, R_2 = R_3 = \text{H}$

5, $R_1 = R_3 = \text{CH}_3, R_2 = \text{OCH}_3$

6, $R_1 = R_2 = R_3 = \text{H}$



7, $R = \text{H}$

8, $R = \text{OCH}_3$

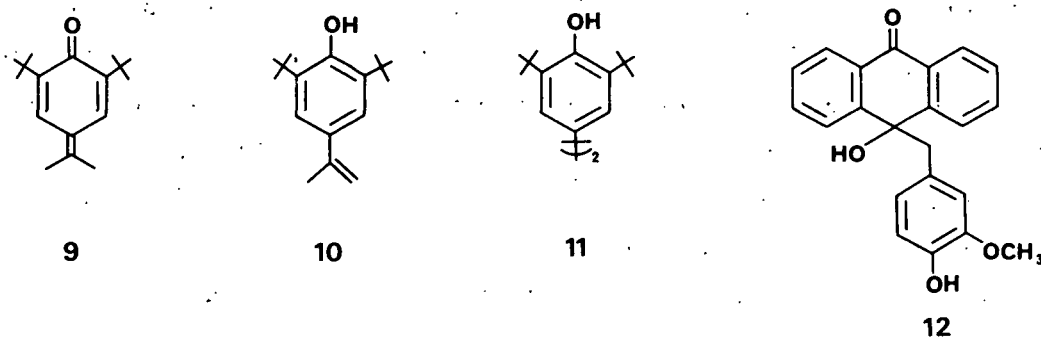
Ideally, we would have preferred to examine the electrochemistry of QMs in pure AN or DMSO; however, two factors prevented this. First, QMs could not be prepared directly in AN or DMSO by the standard procedure because both solvents are water miscible. Second, concentration of the QM/ CHCl_3 solutions (to eliminate the solvent) led to decomposition of the QMs. Therefore, the electrochemical experiments involving the QMs in either AN or DMSO contained 1-5% CHCl_3 . Unfortunately, CHCl_3 is reduced at potentials more negative than -1.5 V (DMSO) or -1.6 V (AN), thus, limiting the useful potential scan range.¹⁰

Besides giving rise to a large interfering cathodic current, the reduction of chloroform produces $^-\text{CCl}_3$, a species which could probably react rapidly with QMs. Chloroform which had been taken through the QM preparation procedure, but in the absence of substrates 4-6, was added to the solvent/supporting electrolyte system, and cyclic voltammograms were recorded. The observed small currents in the region 0 to -1.6 V were indistinguishable from those of pure solvent/electrolyte. Thus, chloroform and by-products of the QM preparation procedure are not electroactive in this investigated potential range.

Quinonemethide 1 produced the cyclic voltammogram shown in Fig. 3A. Only one reduction current peak was observed; at a 0.2

V/sec potential scan rate, the peak potential was at -1.13 V in DMSO and at -1.17 V in AN. [The increase in cathodic current at roughly -1.8 V in Fig. 3 is due to the chloroform reduction.] Similarly, QM 2 gave a single reduction wave with a peak at -1.48 V in AN. Quinonemethide 3 gave an irreversible cathodic current peak at -1.19 V in AN.

The electrochemical behavior of QM 1-3 illustrates that small changes in the QM structure may lead to large changes in the reduction potential. Quinonemethides 1 and 3 differ by a β -methyl group and have similar reduction potentials. However, QMs 1 and 2 differ in the number of substituents on the β -aryl ring and have large differences in reduction potentials. With both ortho positions substituted, QM 2 is probably considerably more hindered than the others and may lack planarity about the α -carbon. Its peak potential is similar to the cathodic peak potential of sterically hindered QM 9.¹¹



The observed QM reduction currents are believed to be due to an addition of one electron to the QM, leading to a quinonemethide radical anion ($QM^{\dot{-}}$). The lack of an anodic current on going from -1.6 to 0 V, even at very rapid (100 V/sec) scan rates, indicates that the $QM^{\dot{-}}$ species are no longer in the vicinity of the electrode to be reoxidized to starting material. In other words, the $QM^{\dot{-}}$ undergoes a rapid chemical reaction prior to the opportunity to be reoxidized. The nature of these reactions will be addressed in a later section.

The addition of 1% water to a solution of QM 1 in AN caused the cathodic peak current intensity to increase by roughly 2.5 times. Further increase in water concentration to about 10% does not alter the cathodic current peak within the experimental error. A current doubling effect upon addition of proton donors is encountered frequently in the reduction of hydrocarbons and ketones (or quinones).^{3,12} It stems from the reduction to the radical anion, followed by coupled chemical and electrochemical reactions. Protonation of the radical anion can be fast; the protonated radical has a higher electron affinity than the parent compound and therefore at the applied potentials easily accepts another electron - a two electron process. Whether current doubling is going to be observed is a function of the basicity of the radical anion.¹²

Few quinonemethides are stable enough to be examined electrochemically; an exception is QM 9. The electrolytic behavior of QM 9 has some similarities to our QMs. Richards and Evans observed a one-electron irreversible reduction of 9 in AN which increased in intensity when water was added.¹¹ The main reaction product of QM 9^{•-} was the dimer 11; basic substances added to the electrolysis also converted some of 9 to a tautomer 10.

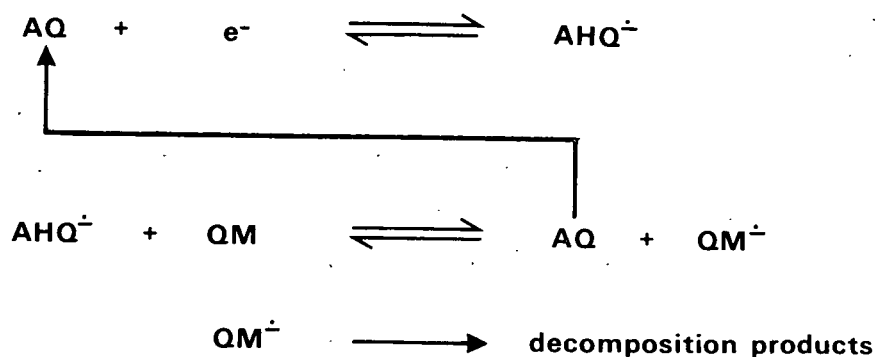
CYCLIC VOLTAMMETRY OF AQ/QM SOLUTIONS

Acetonitrile/chloroform

A solution of AQ in AN was prepared, and its voltammogram was recorded at 0.2 V/sec (Fig. 4, lower curve). Next, a small amount of QM 1 in CHCl₃ was added to the previous solution; another voltammogram was recorded. A second addition of the quinonemethide was carried out, and the voltammogram was recorded again. It can be seen from Fig. 4 that the added QM causes the wave at -0.92 V, associated with the reduction of AQ to AHQ^{•-}, to increase, while the wave associated with the reverse reaction did not increase in intensity. Another important feature is that even at potential scan rates as large as 50 V/sec the wave due to the direct reduction of the QM at the electrode is not observed (no peak at -1.17 V);

thus, the lifetime of the $QM^{\cdot-}$ is shorter than ~ 1 msec.

These results indicate that as the $AHQ^{\cdot-}$ species are formed, they react with QM present in solution, regenerating AQ (and therefore increasing the reduction current) and also depleting QM in the vicinity of the electrode. The "effective" concentration of AQ at the surface of the electrode is increased by the QM reaction, but the combined amounts of $AQ + AHQ^{\cdot-}$ do not change, and hence the anodic wave associated with reoxidation of $AHQ^{\cdot-}$ to AQ is independent of QM level. This process is defined as homogeneous redox catalysis¹³ and has been found in a number of cases involving radical anions such as the reduction of aromatic halides catalyzed by perylene and terephthalonitrile.¹⁴ These reactions can be represented by a simplified scheme:

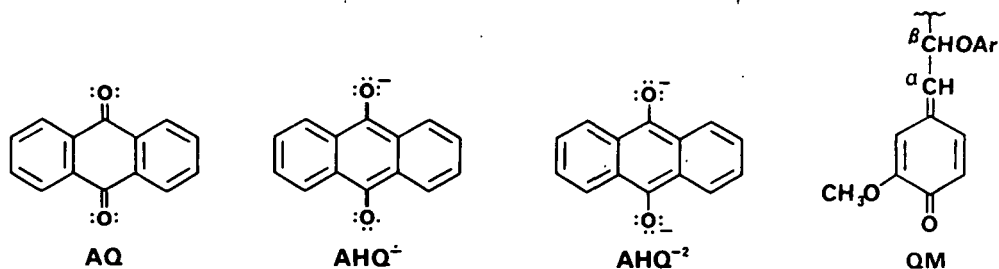


Scheme 1

The rate of electron transfer is a function of the difference in the standard potentials between the anthraquinone and the quinonemethide redox couples. The absolute value of the latter is difficult to estimate because the formation of $QM^{\cdot-}$ is associated with chemical reactions. In general, the larger the separation between the two reduction peaks, the slower the homogeneous electron transfer step.¹³ The rates of the reactions outlined in Scheme 1 are being quantitatively determined and will be the subject of a forthcoming publication.¹⁵

INTRODUCTION

Oxidation and reduction reactions occur during anthraquinone (AQ) wood pulping which result in the production of anthrahydroquinone radical anion ($\text{AHQ}^{\cdot-}$) and dianion (AHQ^{-2}) species.¹ These reduced forms of AQ are believed to interact with lignin quinone-methide (QM) intermediates to cause the lignin to fragment and thereby dissolve in wood pulping liquors.¹



Two basic mechanisms have been proposed for the AHQ/QM interaction. One involves bond formation between the two species to give "adducts" which, if appropriately substituted, can fragment.¹ The other simply involves a transfer of electrons from the AHQ species (anion radical or dianion) to the QM, followed by fragmentation of the QM.¹ Electrochemical experiments are described here which show that $\text{AHQ}^{\cdot-}$ and AHQ^{-2} can interact with quinonemethides by electron transfer and that appropriately substituted quinone-methide radical anions ($\text{QM}^{\cdot-}$) readily fragment.

CYCLIC VOLTAMMETRY

Cyclic voltammetry is a simple, but powerful, technique for adding electrons to (reductions) or removing electrons from (oxidations) certain substrates.² The apparatus consists of a cell containing a working electrode and a counter electrode joined to another compartment containing a reference electrode. A cyclic voltammogram is a measure of current intensity (electron flow) as a function of changes in the applied potential of the working electrode versus the reference electrode. Specifically, in our studies, the potential of the working electrode was increased

A catalytic effect was also observed for mixtures of AQ and QM 2. This model compound is more difficult to reduce than QM 1; the separation between the peak potentials of AQ and QM 2 is 0.56 V (at 0.2 V/sec) compared with 0.21 V in the previous case. The catalytic effect is less pronounced than for QM 1. At fast potential scan rates, two reduction waves, associated with AQ/AHQ⁻ and QM 2/QM 2⁻, were observed. Since the peak separation between AQ and QM 3 is 0.23 V, an efficient electron transfer should occur. Indeed; cyclic voltammograms of AQ and QM 3 were analogous to AQ/QM 1 (Fig. 4).

DMSO/Chloroform

Figure 3B shows the cyclic voltammogram of QM 1 in DMSO before and after the addition of 1/4 of the concentration of AQ used in obtaining the voltammogram shown in Fig. 1. With no interaction between substrates, the AQ reduction current should be ~ 16 μ A. The observed AQ reduction current (35 μ A) was twice the expected value. The presence of QM has caused the regeneration of AQ by reacting with the anthrahydroquinone radical anion. The separation in the reduction waves between AQ and QM 1 in DMSO (0.35 V) is large enough to slow the electron transfer reactions. Indeed, on increasing the potential scan rate, the QM 1 reduction wave can be seen when DMSO is the solvent.

Water/Acetonitrile/Chloroform

The solid curve in Fig. 5 is the cyclic voltammogram of AQ in AN containing 1% chloroform and 2% water. After careful measurement of peak currents, a sample of QM 1 dissolved in chloroform was added to the previous solution. The new cyclic voltammogram showed roughly a quadrupling of the cathodic current at -0.95 V. A doubling of the current can be attributed to water effects on the QM alone. The other twofold increase is attributed to interaction of QM 1 with AHQ⁻ or AHQ⁻² to produce roughly twice the molar amount of electro-active species. Since significant

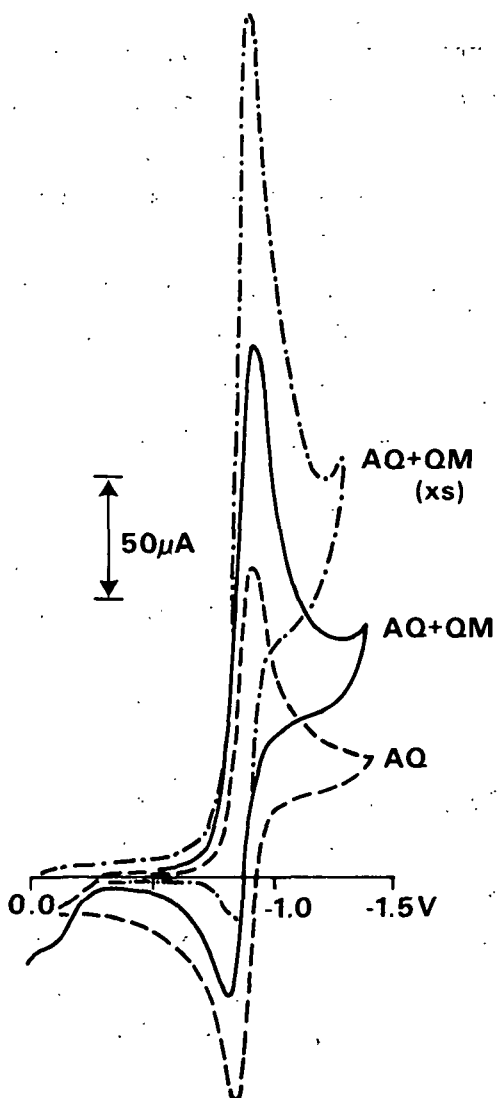


Figure 4. Cyclic voltammograms in AN (10 mL, 0.1M TBAP) of AQ (2.2 mg) alone (---), after the addition of 8 mg of QM 1 in 0.6 mL of CHCl_3 (—), and after the addition of an additional 12 mg of QM 1 in 0.5 mL of CHCl_3 (-·-·-); potential scan rate of 0.2 V/sec.

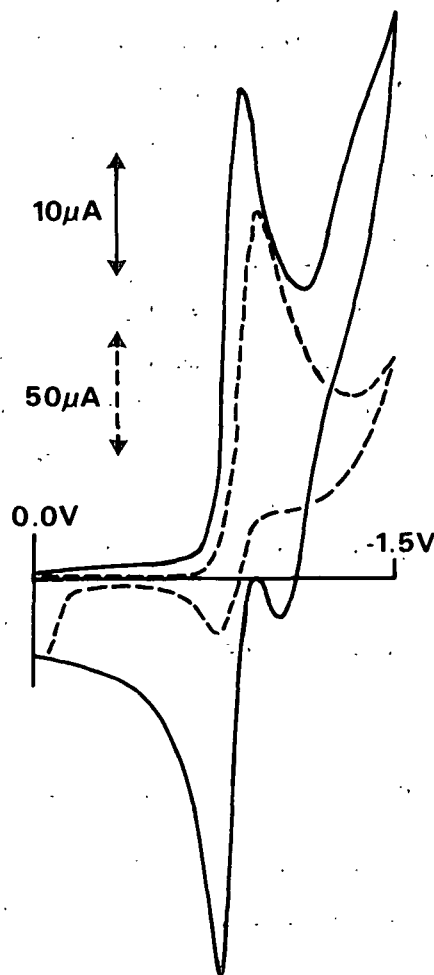


Figure 5. Cyclic voltammogram of AQ (1.3 mg) in AN (10 mL, 0.1M TBAP, 1% v/v CHCl_3 , and 2% v/v H_2O) before (—) and after the addition of 1.5 mg of QM 1 in 0.1 mL of CHCl_3 (---); potential scan rate of 0.2 V/sec. Note that the dotted line curve has a 5 times higher current scale than the solid line curve.

levels of anthrahydroquinone dianion or protonated versions thereof are present in this case, transfer of electrons from AHQ^{-2} species to QM 1 is probably occurring.

Why Not Formation of Adducts?

The term "adduct" refers to the 1:1 addition product which has been observed when a QM is mixed with AHQ^{-2} in water (or aqueous-organic solvents) or when a QM is mixed with unionized AHQ in a pure organic solvent.¹ In the cyclic voltammetric experiments just described, both QMs and AHQ species are present; yet, adducts did not appear to form to any appreciable extent! If stable adducts had formed, there would have been (a) no cathodic current enhancement and (b) a decrease in the anodic, reoxidation wave ($AHQ^{\cdot-}$ or $AHQ^{-2} \longrightarrow AQ$) because the AHQ species would have been consumed in adduct formation reactions. However, the cathodic current was enhanced and the anodic current unaffected.

The cyclic voltammograms of several adducts have been recorded and will be the subject of a future paper. The voltammograms of the adducts (both with and without β -aryl ether bonds) are quite similar and resemble that of anthrone.⁴ As an example, the cyclic voltammograms of QM-AHQ adduct (12)¹⁶ in dry AN and wet AN are shown in Fig. 6. The reduction (of the $C=O$) of the adduct occurs at roughly -1.75 V. The adduct, which is stable for long periods of time in AN, decomposes slightly at potentials > -1.7 V to afford a small anodic peak potential at -0.3 V. The cyclic voltammograms of adducts differ considerably from the cyclic voltammograms of the AQ/QM mixtures.

Why weren't adducts formed during our electrochemical experiments? The answer is not obvious. In the dry acetonitrile experiments, $AHQ^{\cdot-}$ is present and not AHQ^{-2} . Possibly, the reaction between $AHQ^{\cdot-}$ and a QM to give a radical anion adduct, $(QM-AHQ)^{\cdot-}$, is unfavorable. Catalytic currents would have been observed only if $(QM-AHQ)^{\cdot-}$ were to fragment faster than add a second electron to give $(QM-AHQ)^{-2}$, a known stable species. Since it is not exten-

sively resonance stabilized; the $(\text{QM-AHQ})^{\cdot-}$ should readily accept an electron at these potentials.^{3,12,13}

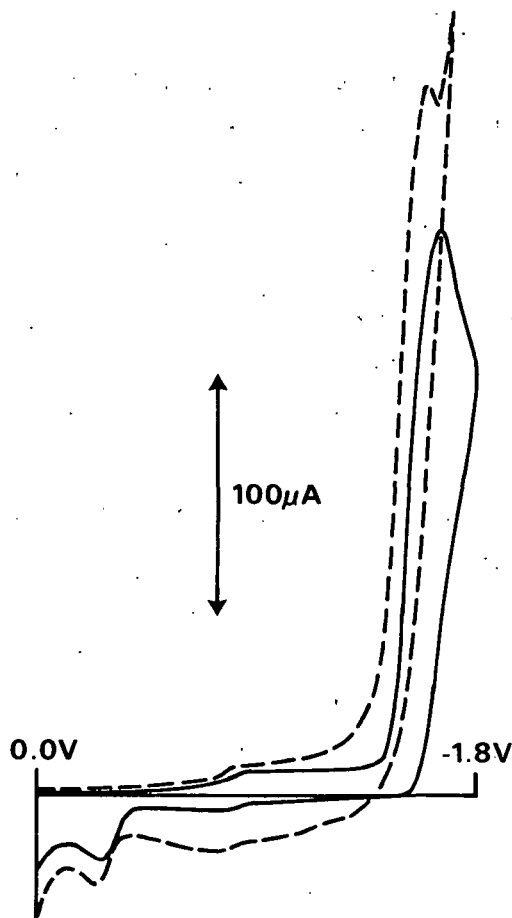


Figure 6. Cyclic voltammogram of QM-AHQ adduct 12 (6 mg) in AN (10 mL, 0.1M TBAP) before (—) and after addition of 1% water (---); potential scan rate of 0.2 V/sec.

In the aqueous experiments, both $\text{AHQ}^{\cdot-}$ and AHQ^{-2} , and protonated versions of each, are present together. Possibly, electron transfer to a QM from $\text{AHQ}^{\cdot-}$ (or one of the protonated species) occurs at a faster rate than adduct formation between the QM and AHQ^{-2} (or a protonated version thereof.) The relative rates of the two processes are the important parameters, as well as the activation energies involved in these reactions. We are continuing to carry out experiments in which the rate of electron

transfer reactions can be obtained from a mathematical treatment of the electrochemical results. They will shed light on the quantitative aspects of these reactions and possibly allow extrapolations of the results to higher temperatures.

PREPARATIVE ELECTROLYSES

Micropreparative electrolyses (ca. 40 mg of substrate) were performed on individual solutions of AQ and QM 1 and a mixture of AQ and QM 1. In these experiments the solution was stirred during the electrolysis, the potential was held at some fixed value, and the electrode had a large surface area. The anolyte and catholyte were separated by a cation permselective membrane pretreated in such a way as to allow fast neutralization of base by acid generated in the anode compartment. It is imperative that the cathode and anode be separated, but at the same time the pH at the cathode compartment remains as close to neutral as possible. The QM lifetime will decrease substantially at high pH values, since good nucleophiles will be present.

The preparative electrolysis of anthraquinone alone in acetonitrile at -0.9 V produced a strong red color (associated with AHQ^- production). However, an identical electrolysis of an acetonitrile-5% chloroform solution of AQ and QM 1 exhibited no red color in the initial phase. When the QM had been substantially consumed, the red color appeared. During the coelectrolysis the monitored current was constant while QM was present; as soon as color developed in the solution the current decayed. At -0.9 V the QM 1 per se is not electroactive.

The preparative coelectrolysis solution was analyzed by gas chromatography/mass spectroscopy (GC/MS) during the course of the reaction. In addition to AQ, only two other products were observed in any appreciable amounts. These products, guaiacol 13 and isoeugenol 14, were identified by direct comparison with authentic samples. Table 1 shows the relative amounts of guaiacol and isoeugenol formed as a function of time in the coelectrolytic

experiments. Since the decomposition of the QM by nucleophiles could lead to the same products, extreme care was taken that the amounts in the table reflect electrochemically induced decomposition reactions.

Preparative electrolysis of QM 1 at -0.9 V did not show an increase in the amount of guaiacol and isoeugenol other than that expected by the time elapsed between the starting electrolysis and final electrolysis. Substantial electrolytic currents and decomposition of QM into guaiacol, isoeugenol, and other species occurred only at potentials of -1.1 V or more negative values. It is likely that dimeric products were also formed. Detailed analysis of products will be published later.

TABLE 1
PHENOL PRODUCTION IN THE COELECTROLYSIS OF QM 1 AND AQ

Coelectrolysis 1			
Charge, Coulombs	Guaiacol, ^a mM	Isoeugenol, ^a mM	Amount Expected, ^c mM
blank ^b	0.7 ± 0.2 ^b	0.6 ± 0.2 ^b	0.0
4.2	1.4 ± 0.4	1.1 ± 0.4	1.5 ± 0.1
15.0	3.4 ± 0.9	3.2 ± 1.0	5.4 ± 0.3
18.0	5.0 ± 1.3	5.7 ± 1.7	6.4 ± 0.4
Coelectrolysis 2			
Charge, Coulombs	Guaiacol, ^d mM	Isoeugenol, ^d mM	Amount Expected, mM
0.0	0.00	0.00	0.00
2.2	0.40 ± 0.15	0.15 ± 0.05 ^e	0.8 ± 0.1
5.0	1.00 ± 0.25	0.60 ± 0.18 ^e	1.9 ± 0.2
10.0	2.50 ± 0.50	1.60 ± 0.48 ^e	3.7 ± 0.3

^aApproximate concentration of guaiacol and isoeugenol determined by GC/MS single ion monitoring, relative to the anthraquinone concentration at 5.0 ± 1 mM, from a micropreparative electrolysis at -0.85 V in acetonitrile.

^bSample of QM 1 + AQ left overnight in AN/0.1M TBAP.

^cAssuming an 80% yield of QM 1 from 4; this sort of yield has been observed by us using NMR analysis.

^dDetermined by GC/MS with anisole internal standard. Average anthraquinone concentration determined by GC/MS throughout the electrolysis was 5.0 ± 1 mM. Micropreparative electrolysis at -0.90 V in acetonitrile.

^eThe lower isoeugenol yields may be due to polymerization reactions.

In essence, the proposed chemistry occurring during coelectrolysis of AQ/QM 1 is as follows: $AHQ^{\cdot-}$, generated by heterogeneous electron transfer from the electrode to AQ, rapidly transfers an electron to the QM and the resulting species, $QM^{\cdot-}$, fragments to yield most likely guaiacol anion and the stabilized α -radical, which is reduced further (probably by $AHQ^{\cdot-}$) to isoeugenol anion (Scheme 2). The net reaction, which is summarized in reaction 5, is not possible (at -0.9 V) without the present of AQ.

The results of the micropreparative electrolysis cannot be reconciled by an adduct mechanism. An adduct between QM 1 and AHQ^{-2} would be expected to produce guaiacol and isoeugenol upon warming in aqueous alkali but not in a neutral solution at room temperature.¹ The voltammetric experiments with a stable adduct (Fig. 6) do not show fast fragmentation of the adduct electrochemically. In fact, the anodic scan following the carbonyl reduction shows very little decomposition to AQ.

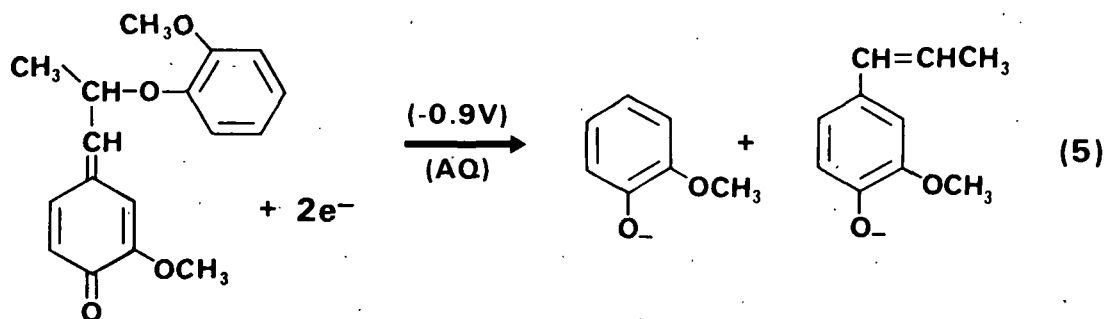
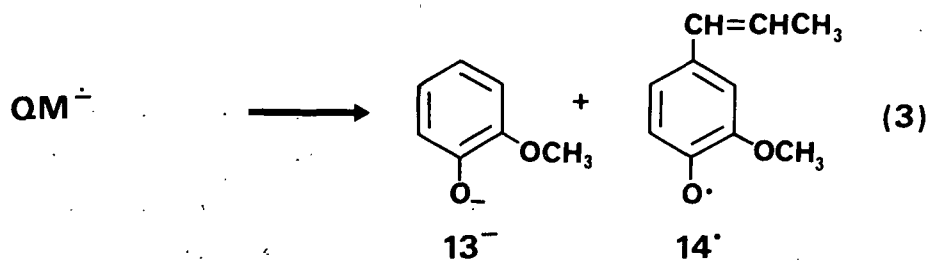
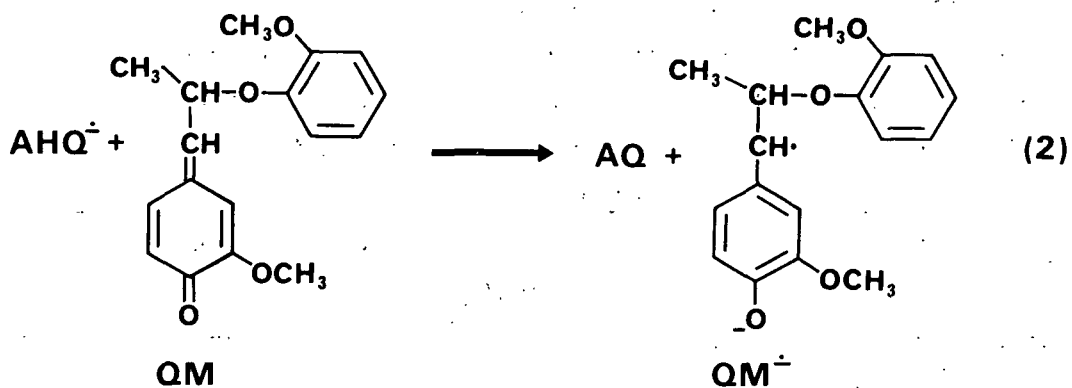
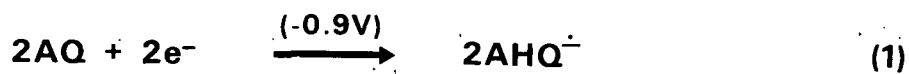
CONCLUSIONS

The electrochemical experiments described here demonstrate that β -aryl ether lignin model quinonemethides accept electrons from reduced anthraquinone species and then rapidly fragment at the β -linkage to phenolic products. In the time scale of the voltammetric experiments the electron transfer reactions appear to occur in preference to adduct formation reactions. Also, the electron transfer reactions give products identical to those produced from "adduct decomposition reactions."

When the two reactants have similar reduction potentials, the electron transfer step between $AHQ^{\cdot-}$ and AHQ^{-2} with a QM is very fast and efficient. Reduction potentials appear to vary with the structure of the QM (and presumably also with AQ structure) and the solvent. Exactly how efficient electron transfer reactions might be with actual lignin QMs in water at 170°C is not known.

One must keep in mind that conclusions based on electrochemical experiments done at room temperature in organic or aqueous-organic solvents with soluble models may not accurately describe

Scheme 2



the pulping of wood in water at high temperatures. Even so, the electrochemical studies do establish that electron transfer reactions of quinonemethides can lead to efficient ligninlike fragmentation, a fact which may change the way wood chemists attack the problem of improving wood pulping systems. Future studies will be aimed at establishing the importance of electron transfer reaction under more typical pulping conditions.

EXPERIMENTAL

The NMR spectra were obtained using a JEOL FX 100 spectrometer. A Hewlett-Packard model 5985 GC/MS spectrometer, using an SP-52 metal column was employed in the quantitation of phenolics. The cyclic voltammetric experiments employed an EG&G Princeton Applied Research Corp. potentiostat (model 173D) with a universal programmer (175); slow scan rate results were recorded with a Hewlett Packard XY recorder model 7046 A. Faster scan rate experiments were recorded on a Bascom-Turner recorder (model 4120) and stored on discs.

Quinonemethide 1. Quinonemethide 1 was prepared according to the method of Ralph and Young,⁸ starting with model 4.¹⁷ A NMR spectrum of 1 in CDCl₃ agreed with the reported spectrum.⁹ The spectrum remained unchanged after weeks in the sealed NMR tube.

Quinonemethide 2. Quinonemethide 2 was prepared according to the method of Ralph and Young,⁸ starting with model 5.¹⁸ A NMR spectrum of 2 in CDCl₃ showed signals (δ values) at 1.53 (d, J = 6.4 Hz, γ A-CH₃), 1.55 (d, J = 6.4 Hz, γ S-CH₃), 2.26 (s, S&A aryl CH₃), 3.62 (s, 3S-OCH₃), 3.74 (s, 3A-OCH₃), 3.76 (s, 2'/6'S-OCH₃), 3.77 (s, 2'/6'A-OCH₃), 5.17 (q, J = 6.4 Hz, β A-H), 5.26 (q, J = 6.4 Hz, β S-H), 6.32 (s, 3'/5'A&S-OCH₃), 6.1-6.6 (m, 2A&S, 5A&S, α A&S protons), 7.00 (d of d, J = 9.6 and 2.2 Hz, 6S-H) and 7.23 (d of d, J = 0.6 and 2.4 Hz, 6A-H); the symbols A and S stand for anti and syn isomers.⁸ The NMR integration areas match perfectly for the proposed structure and indicated a 2:1 ratio of syn to anti isomers.

Quinonemethide 3. Quinonemethide 3 was prepared by the method of Ralph and Young,⁸ starting with model 6.

Quinonemethides 7 and 8. Syringyl alcohol in CDCl_3 was treated with BrSiMe_3 and Na_2CO_3 in an attempt to prepare quinonemethide 8. Analysis of the resulting deep red-colored solution by NMR and GC/MS showed that dimerization had occurred. The major product was $\text{S-CH}_2\text{-CH}_2\text{-S}$ (mol. ion at $\underline{m/e}$ 334 and a large signal at $\underline{m/e}$ 167 in the MS); the minor product was S-CH=CH-S (mol. ion at $\underline{m/e}$ 332). Here the symbol S stands for a 3,5-dimethoxy-4-hydroxy-phenyl group.

A similar treatment of vanillyl alcohol did not give QM 7, but rather a complicated mixture of condensation products.

Cyclic Voltammograms. The cyclic voltammograms were obtained using a Pt bead working electrode or a planar platinum disk electrode, surrounded by a Pt coil secondary electrode; the reference electrode used was a Ag/AgCl or a Ag/Ag^+ reference electrode. The solvents AN and DMSO were used as supplied by Burdick and Jackson (spectroscopic grade, for liquid chromatography; the newest lots available). Single sweeps were analyzed; the cell was flushed with nitrogen gas (99.99%) presaturated in acetonitrile between runs. Multiple sweeps were also employed, as well as runs following potentiostatic short electrolysis at preestablished potentials to indicate the nature of possible reaction products. The electrodes were mechanically and electrochemically pretreated.

Blanks were obtained with the solvent (or solvents) with 0.1M tetrabutylammonium perchlorate first, to indicate that they were electrochemically pure and suitable for further investigation of AQ or QM or both. Blanks were also obtained as a function of chloroform and water concentrations.

Micropreparative Electrolyses. In micropreparative electrolyses about 40 mg of the quinonemethide was added to a three electrode cell with cathodic and anodic compartments separated by means of a Nafion-127 (in the H^+ form) cation exchange membrane. The reference electrode compartment ends in a Luggin capillary near

the working electrode.¹⁹ The working electrode was a platinum mesh, and a platinum coil secondary electrode was placed in the Teflon auxiliary electrode compartment, which ends in the ion exchange membrane. The pretreatment of the membrane is as follows: after being placed in the Teflon compartment the membrane was soaked for one hour in boiling aqueous acid; the membrane is then placed in an acetonitrile solution containing the supporting electrolyte and boiled in the solution for another hour. The cell was maintained at all times under a nitrogen atmosphere and was stirred to improve mass transfer. The charge passed was recorded in a PARC digital coulometer model 179. Small samples (less than 0.5 mL) were removed at various times for GC/MS analyses. The total volume of the cell was less than 20 mL.

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